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METAL HYDRIDE MATERIALS PROGRAM AT BNL - CURRENT STATUS AND FUTURE PLANS+

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Over the past year, our materials development program has been focused on a number of areas. These include the effect of a third alloying metal on the properties of iron titanium hydride, the effect of alloy microstructure on hydride properties, the change in activity of pertinent alloys towards hydrogen as a function of the number of hydriding-dehydriding cycles, the poisoning effect of O_2 in the hydrogen gas and the outgassing temperature required to activate virgin materials. Several of these areas have been covered in detail recently and will not be referred to here (1), (2). Our attention at this meeting will center on unreported data involving both ferrotitanium and other alloys and a discussion of our future plan of work.

High Cycle Testing: In addition to pressure-temperature-composition relationships there exist many other system properties which are important with respect to the performance of a practical hydrogen storage reservoir. Perhaps the most important of these are:

(1) the change of activity of the alloy toward hydrogen as a function of the number of such cycles,

(2) the physical attrition of the alloys as a function of the number of hydriding-dehydriding cycles, and

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(3) the poisoning effect of impurities such as O_2, N_2, CO, etc., in the hydrogen gas.

In order to investigate these variables a laboratory high cycle test apparatus was built. This system was capable of subjecting simultaneously three alloy samples to five complete hydriding-dehydriding cycles per hour with a composition swing per cycle of 1 H/Ti unit. Our initial objective was to determine whether there is any inherent deterioration of FeTi or similar materials as a function of hydriding-dehydriding cycles when pure hydrogen is used. The data shown in Table 1 establish that no such deterioration occurs.

Table 1

High Cycle Test

Material	Complete Cycles	Temperature Change/Cycle °C, Avg.	Pressure Change/Cycle Psia, Avg.	Composition Change/Cycle ΔH/Ti, Avg.
FeTi	19568	-1 to +100	428-459	1.11
$TiFe_{.79}Mn_{.15}$ (INCO #2)	28411	-1 to +100	179-211	1.08
$TiFe_{.76}Mn_{.14}$	26319	-1 to +100	87-114	0.96

The high cycle apparatus was also used to measure the effect of O_2 in the hydrogen gas phase on the reactivity of FeTi towards hydrogen. The results of these experiments are summarized in Table 2.

Table 2

Poisoning Effect O_2 in H_2

Initial O_2 Conc. in H_2	% Reduction in Composition Change (ΔH/Ti) Cycle	
Mol %	After 5 Cycles	After 40 Cycles
1.10	90	90
0.10	40	80
0.01	6	20
0.001	2	9

As expected these data indicate that FeTi is very sensitive to the presence of oxygen (which may be converted to H_2O) in the gas phase. However, in all cases it was possible to restore the alloy to its original activity by subjecting it to the usual activation procedure.

With respect to the rate of physical attrition (Table 3), the highest rate occurs in the first few cycles after which it slows considerably. It is also apparent that pure FeTi is much more resistant to physical attrition than any of the ternary manganese alloys tested. In this connection, it should be noted that the FeTi sample was finally removed after 19,568 cycles. Qualitative examinations indicated that while a substantial decrease in particle size occurred, it was not of a magnitude which would constitute a serious engineering problem. This sample is now undergoing extensive physical and chemical characterization.

Table 3

Particle Size Distribution

$TiFe_{0.7}Mn_{0.18}$ (INCO #1) and FeTi (NL-2)

As a Function of Hydriding-Dehydriding Cycles

Screen Classification, Mesh	Weight Percent		
	$TiFe_{0.7}Mn_{0.18}$*		FeTi*
	5 Cycles	1115 Cycles	5478 Cycles
+ 16			11.4
+ 20			2.9
+ 30			2.1
+ 40			4.3
+ 60	5.3	6.4	14.7
+ 80	2.0	0.6	16.4
+100	1.5	2.1	11.0
+140	10.1	12.4	
+200	32.2	25.5	23.0
+275	19.3	21.5	4.2
+325	17.1	11.8	2.3
-325	14.1	19.7	7.7

* Initial particle size range -10 +16 (U.S. Standard Sieve).

Activation

The usual procedure for activating FeTi specifies high temperature outgassing (300°C). Such a requirement can impose difficult problems in large hydride reservoirs where activation in situ is desirable. Thus a series of experiments were carried out with manganese containing ferrotitanium alloys to determine minimum activation temperatures. This alloy type was chosen because it is of interest for our particular purpose (stationary storage) and also because it was apparent from our previous work that such alloys could be readily activated. The results of this work are shown in Table 4.

Table 4

Low Temperature Activation Experiments

Sample	Maximum Temperature (°C)	Elapsed Time at 500 psi (hr)	Final H/M
$TiFe_{0.7}Mn_{0.2}$	50	3.5	0.94
$TiFe_{0.9}Mn_{0.1}$	25	27.5	0.98
$TiFe_{0.85}Mn_{0.15}$	25	19.0	0.98
$TiFe_{.70}Mn_{.18}$ (INCO #1)	25	25	0.91

Current and Future Work

The primary goal of the Brookhaven Metal Hydride Development Program has been revised. Simply stated it is to discover and develop new metal hydride compounds having thermodynamic properties similar to that or iron titanium hydride, but with significantly greater hydrogen fuel storage capacities and which would be attractive for automotive applications.

Our investigation will be concerned primarily, but not exclusively, with two separate alloy systems, i.e., those of magnesium and titanium. Currently, three Mg alloys are of interest as lightweight hydrogen storage media; i.e., Mg_2Ni, Mg_2Cu and magnesium itself, catalyzed with a small amount of Ni or Cu. Unfortunately, all of these hydrides require relatively high decomposition temperatures, the most favorable case being the Mg_2Cu-H system which has a dissociation temperature (the temperature at which equilibrium dissociation pressure is 1 atm) of 239°C. All of these systems were defined several years ago (3). Since that time, a large number of lightweight alloys have been examined, but none were found to be more attractive for automotive storage (4). Nevertheless, a re-examination of certain low melting alloys, of the type MgM_x may be profitable. Such alloys were originally investigated using accepted alloy activation techniques, i.e., outgassing and contacting the sample with H_2 at temperatures which were high relative to the melting point of the alloy. Under such conditions the metal atoms have appreciable mobility and if a hydride phase forms, it is likely to be the phase which is most thermodynamically favored; i.e., MgH_2 rather than a less stable ternary hydride system. A known example of such disproportion is as follows:

$$2Mg_2Cu + 3H_2 \rightleftharpoons 3MgH_2 + MgCu_2$$

Thus, we will re-examine such alloys using a new approach, i.e., a low temperature activation technique. Such a procedure, if successful, could result in the syntheses of several ternary alloy hydrides having properties substantially more attractive for our purpose than any currently available.

In the case of titanium alloys, the same considerations hold, particularly for those that are titanium rich (e.g., Ti_2M type). We have also recently noted (5) the existence of a novel hydride having a composition corresponding to $TiCr_2H_{3.7}$. This material, originally discovered as part of our fundamental research program* is interesting in several respects; it contains 2.4 wt % H, the presence of Cr enhances the hydrogen sorption capacity and it is

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extremely unstable as shown by the thermodynamic data listed in Table 5. In fact, it is probably too unstable for automotive purposes, but it may represent a new class of hydrides, the properties of which can be modified by the addition or substitution of a third metal component. Indeed, we have preliminary data (Fig. 1) supporting this contention in which Mn is substituted for Cr to give an alloy composition corresponding to TiCrMn.

Table 5

Relative Partial Molal Quantities Per Gram-Atom of Hydrogen (298 °K) for the Formation of $TiCr_2H$ from $TiCr_2$

Comp.	$(\bar{H}_H - \frac{1}{2}H^{\circ}_{H_2})$	$(\bar{S}_H - \frac{1}{2}S^{\circ}_{H_2})$	$(\bar{F}_H - \frac{1}{2}F^{\circ}_{H_2})$	A^a	B^a
$TiCr_2H_{0.90}$	-1.81	- 9.1	+0.91	-1824	+ 9.1927
$TiCr_2H_{1.50}$	-2.49	-13.2	+1.45	-2502	+13.3014
$TiCr_2H_{2.10}$	-2.55	-13.8	+1.56	-2562	+13.8620
$TiCr_2H_{3.30}$	-2.21	-15.0	+2.25	-2224	+15.0794

[a] Constants in the equation $\ln P_{atm} = (A/T) + B$.

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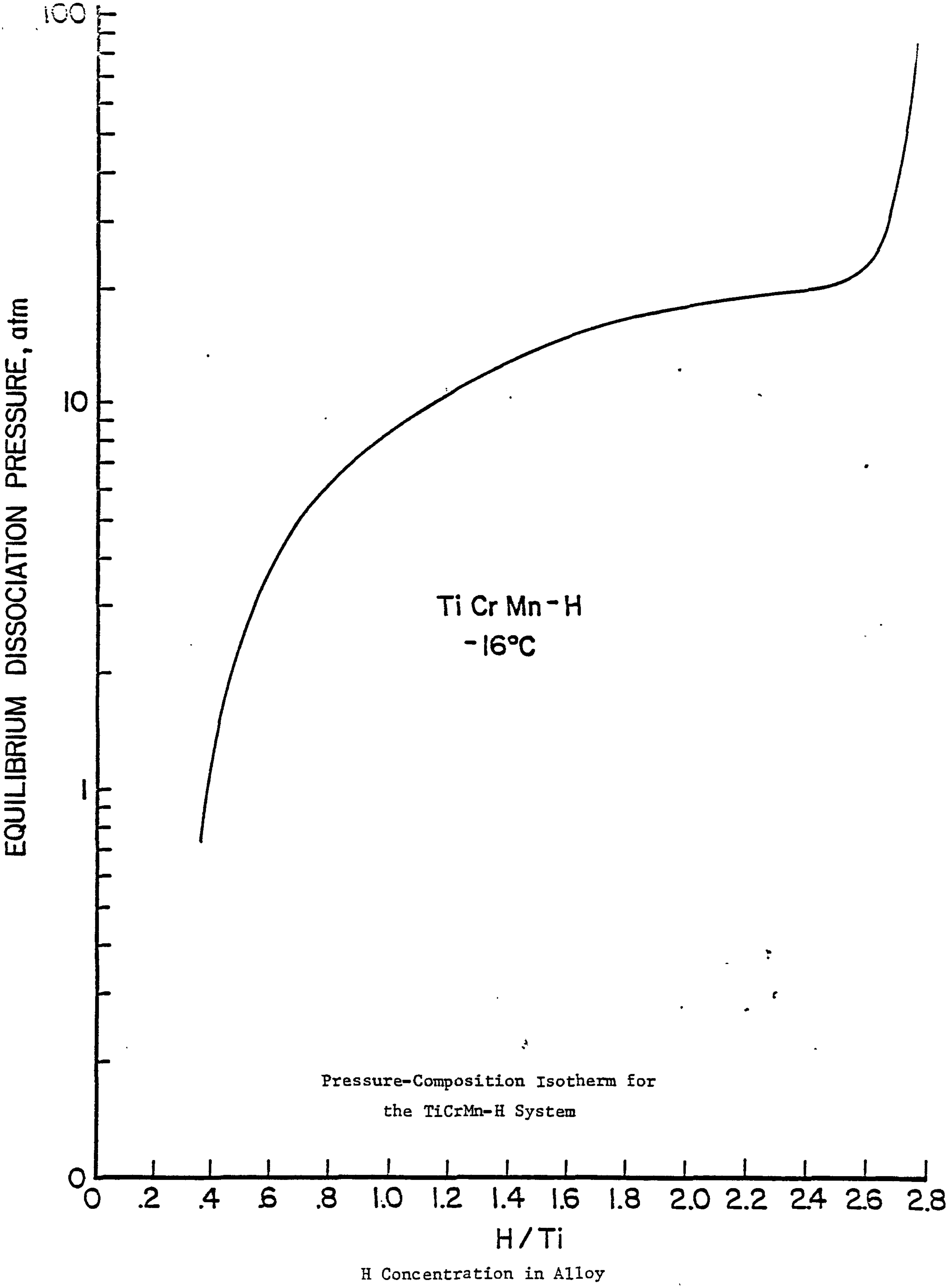

Pressure-Composition Isotherm for
the TiCrMn-H System

H Concentration in Alloy